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(54) Floor treatment product.

(57) An emulsified, balanced floor treatment product is provided having a plurality of cleaning agents, including acids, alcohols, hydrocarbon solvents, water, a plurality of silicone components, at least one fluorosilicate compound capable of reacting with calcium carbonate, and at least one emulsion-stabilizing agent.

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FLOOR TREATMENT PRODUCT

RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Application Serial No. 852,361 filed April 15, 1986, the disclosure of which is expressly incorporated herein by reference in its entirety

FIELD OF THE INVENTION

The present invention relates to compositions for the treatment of hard surfaces, such as floors, which are effective to clean, polish and protect such surfaces, and particularly to compositions comprised of an acid/silicone base formulation.

BACKGROUND OF THE INVENTION

Historically, architectural developments as embodied in residential and commercial buildings and edifices of other purposes have been accompanied by the need to clean and protect the various surfaces of such architectonic expression. The present invention relates to the treatment and maintenance by a single product of floors, walls, stairs, patios, walkways and other hard and substantially smooth surfaces for the purposes of cleaning, polishing and protecting them from wear and weathering. As will be apparent from the following, the present invention may be broadly applied to a variety of surfaces; however, the term "floor" will be utilized hereinafter for convenience in collectively referring to all appropriate surfaces.

The present invention relates particularly to a product for treating and maintaining floors and more particularly to a product for treating and maintaining floors having a surface material which is hard and smooth. Representative floor surfaces include those made of metal such as steel, or stone such as natural or reconstituted marble, ceramics such as terracotta, as well as surfaces bearing an organic-based coating such as plastic sheets or acrylic tile, and even to surfaces covered with wood parquet. Fibrous materials, however, such as carpets and rough surfaces such as concrete are not hard and substantially smooth as contemplated herein, and are therefore inappropriate surfaces for treatment with the products of the present invention.

The traditional approach to floor treatment involves a multi-step procedure. Floors are initially

exposed to a protecting agent which forms an interface between the floor and the air or objects which pass over or rest upon the surface. Ideally, the protective interface will also impart an acceptable shine to the floor. Subsequent "maintenance" steps involve the cleaning, polishing and continued protecting of the treated floor.

In some cases, for example, involving floors or surfaces of natural stone or marble, such as "comblanchien" or travertine or terrazzo, the basic treatment traditionally involves the production of a chemical reaction, commonly called crystallization, which leads to the formation of a hard, shiny superficial layer on the marble surface (i.e., calcium carbonate or CaCO_3). This reaction occurs according to the known reaction scheme: $\text{SiMgF}_6 + 2\text{CaCO}_3 \rightarrow \text{SiO}_2\text{MgF}_2 + 2\text{F}_2\text{Ca} + 2\text{CO}_2$. To minimize reactivity if desired, SiNa_2F_6 can be used in place of SiMgF_6 . Other surfaces that expose mineral substances, such as composite vinyl flooring, react similarly. In the case of floors having an organic coating such as plastic, the basic treatment consists of the application of a varnish or film-forming compound. The ultimately-desired shining appearance then results from a polymerization of the treatment product itself without the necessity for chemical reaction with the floor surface. Alternatively, for chemically inert floors such as wood or thermosetting plastics, an acrylic-based layer can be formed for protection purposes.

Generally, maintenance consists of a cleaning or scouring step, followed by the reapplication of a shiny and/or protective layer and subsequent polishing thereof. Future maintenance of a treated floor thus provides maintenance and/or restoration of the foregoing protective layer, unless the residuum of the floor treatment product is stripped down to the actual floor surface, as may periodically be necessary or desirable. The traditional maintenance scheme involves a "spray" step which involves spraying, onto the surface to be treated, an appropriate composition followed by the mechanical actions of brushing or polishing, advantageously accomplished with the aid of a floor polishing machine.

It is understandable that floor treatments which differ so widely in substrate and in protecting versus maintaining mode of action similarly require a variety of quite different products in order to properly attend to their care. The present invention relates to compositions which exhibit a polyvalent action in the sense that they are useful for the treatment of all surfaces, such as floors, having a hard and substantially smooth surface regardless of the compositional nature of such surfaces. The

present invention further relates to products which accomplish protecting through chemical reaction or otherwise, cleaning, polishing and maintaining in one step.

A wide variety of useful floor treatment compositions are known. Such products may include, for example, a cleaning ingredient such as an acid mixed together with a silicone capable of imparting water repellancy as well as an enhanced shine to the floor surface so treated. The complete compositions formulated from such a base may be critical, however, as they will vary in substrate specificity, efficacy, odor and even in flammability. For example, U.S. Patent No. 3,681,122 to Domicone et al. and Canadian Patent No. 843,388 to Hyde disclose abrasive silicone-containing cleaning and conditioning compositions. While these compositions are effective for cleaning and conditioning glass-ceramic surfaces, they have certain unsatisfactory properties for more broad-based applications. For example, when the compositions contain a soluble alkaline metal silicate they are useful for cleaning glass-ceramic surfaces which have been stained, but the surface maintains and develops a stubborn stain over a period of time from the treatment product. If an analogous composition is utilized which is free of the soluble alkaline metal silicate, it is effective for protecting the glass-ceramic surface without causing further stain but it also lacks the cleaning power to remove the old stain.

U.S. Patent No. 3,579,540 to Ohlhausen relates to a method for treating nonporous substrates with acid-silicone products to protect and render them water repellant. The compositions therein disclosed comprise a mineral acid such as sulfuric acid, phosphoric acid, aromatic sulfonic acids, aliphatic sulfonic acids and hydrochloric acid. The silicone reagent disclosed by Ohlhausen also includes an alkylpolysiloxane such as dimethylpolysiloxane, methylhydrogenopolysiloxane and methylphenylpolysiloxane. Solvents, diluents and extenders such as alcohols, chlorinated hydrocarbons, ethers, ketones, esters, aromatic hydrocarbons, water, colloidal pyrogenic silicas and clays are also disclosed as additional ingredients. Such formulations are relatively limited in their applicability in the absence of the ability to form protective layers through mineral reacting components or acrylic copolymers, and in the absence of additional emulsifying agents. Furthermore, pure organic acids possess advantageous cleansing activities.

To the foregoing general type of formulation is included a surfactant by some workers in the field. Thus, for example, U.S. Patent No. 4,212,759 to Young et al. discloses an acidic cleaning composition comprising an acid-stable hydrocarbon-and-water emulsion which contains a liquid hydrocar-

bon, a solid porous absorbent, and a minor amount of an acid to provide an acidic emulsion. The formulation may also contain a soap or detergent, and a minor amount of a polysilicone or a thickening agent. Preferred acids include oxalic acid, sulfamic acid and the like. The compositions of Young et al. contain polysilicones as a surface-treating agent to give a smooth feel to the surface treated and to help protect this surface from soiling due to dirt, spills, and the like. Suitable polysilicones include polydimethylsiloxane. The compositions disclosed may also include a porous absorbent present in an amount sufficient to stabilize the emulsion, and which may also enhance the cleaning activity of the compositions disclosed by acting as an abrasive. Such formulations, however, act primarily as a cleaning or maintaining agent rather than a protecting agent in the absence, for example, of mineral-reacting components and acrylic copolymers. The use of an acid only to form an acidic emulsion does not appear to provide the cleansing efficacy of other acid cleaners.

U.S. Patent No. 4,124,523 to Johnson discloses silicone-containing acidic cleaners which consist essentially of polydimethylsiloxane, water, acid, abrasive and colloidal silica flocculated with a non-ionic surfactant. The particular acid components are said not to be critical and may include oxalic acid, phosphoric acid, acetic acid, citric acid and hydrochloric acid. Suitable silicone components include methyl-endblocked, hydroxyl-endblocked and methyl-and hydroxyl-endblocked polydimethylsiloxanes and mixtures thereof, and the polydimethylsiloxane fluid may be present in the form of an emulsion. A suspending agent or emulsifier may be used to properly disperse the polydimethylsiloxane fluid in the aqueous phase. Johnson also discloses that any of the well-known nonionic surfactants may be used in the compositions taught. Finally, the compositions disclosed may also include an abrasive such as diatomaceous earth, aluminum oxide, ground quartz, tripoli and talc. Again, such formulations are primarily cleaners rather than protecting treatments.

A variety of other formulations are also known. U.S. Patent No. 3,095,381 to Tinnon et al. discloses a hard surface cleaning composition containing an alkyl-substituted tertiary acetylenic hexynol which additionally contains an organic solvent, isopropyl and diethylene glycol monoethyl ether, as well as non-volatile surfactants. U.S. Patent No. 4,689,168 to Requejo discloses a hard surface cleaning composition comprising an organic polar solvent, a volatile organosiloxane and a volatile surfactant such as an acetylenic alcohol or diol. An acidic component is not taught by Requejo. An alternative formulation is taught by U.S. Patent No. 4,311,608 to Maurice which discloses an all-purpose cleaner

consisting essentially of isopropyl alcohol, linear dodecylbenzene sulfonic acid, a primary alcohol and an average of about 6 moles of ethylene oxide per mole of alcohol, a second primary alcohol and an average of about 2.5 moles of ethylene oxide per mole of alcohol, sodium lauryl sulfate and dimethylpolysiloxane.

U.S. Patent No. 3,992,235 to Denissenko et al., the disclosure of which is expressly incorporated herein by reference in its entirety, relates to a composition capable of shining the surface of a substrate such as a wood parquet floor without prior stripping and without subsequent polishing, by simply applying and drying the composition on the surface. The composition is an anhydrous solution comprising at least six and preferably seven constituents which consist, in critical proportions, of a solid film-forming macromolecular compound, a hard resin, a liquid plasticizer, a solid plasticizer and a solvent mixture consisting of at least one lower alkanol. The seventh, optional component may be a silicone oil.

Certain cleaning acids may also be undesirable in particular formulations, as explained in U.S. Patent No. 4,013,579 to Nakasone et al. which discloses an acidic cleaning composition comprising at least one member selected from the group consisting of furan-carboxylic acid and derivatives thereof and tetrahydrofuran-carboxylic acid and derivatives thereof. Nakasone et al. teaches that a variety of acid substances are effective cleaning agents, including oxalic acid, but teaches that such substances have significant toxicity and/or smell disadvantages. It was therefore a primary object of the composition disclosed by Nakasone et al. to provide an acidic cleaning composition in which the disadvantages of conventional acidic cleaners are greatly reduced. Thus, this patent teaches that oxalic acid, while an effective spot remover, has a very high toxicity and a high skin penetrating property and therefore that the use of oxalic acid-containing compositions is undesirable. Notwithstanding the teachings of Nakasone et al., the use of acidic components such as oxalic acid is generally considered to be desirable by those skilled in the art for their superior cleansing efficacies.

What is desirable in a floor treatment product, therefore, is a formulation applicable to a wide variety of floor surfaces which, furthermore, protects and maintains in a single formulation and which also falls within acceptable limits on corrosivity, flammability, odor and slipperiness. It is thus an object of the present invention to provide a complete floor treatment composition which is polyvalent in the sense that it possesses a broad applicability to a variety of surface compositions. It is a further object of the present invention to provide a floor treatment composition that is advanta-

geously formulated for its efficacy, acceptable odor and compliance with U.S. flammability regulations and other safety considerations. Also, an object of the present invention is a floor treatment composition which protects both calcium carbonate-containing as well as nonmineralized floors; effectively cleans hydrophilic as well as hydrophobic dirt and stains and imparts a shine to a surface, all in one solution. Additionally, the composition is acceptable for daily or routine maintenance and avoids the need for separate stripping and polishing products.

SUMMARY OF THE INVENTION

The foregoing objects are accomplished by the present invention which, per gallon formulated (or about 3,776 ml), forms an emulsion which comprises the following ingredients: a polycarboxylic chelating acid, a plurality of silicones including at least one aminofunctional polysiloxane and preferably at least one silane, an alkaline earth fluorosilicate and an acrylic resin; a co-solvent system which includes at least one lower aliphatic alcohol, glycol ether, halogenated hydrocarbon and nonhalogenated hydrocarbon solvent, and water; and as additives, preferably, a perfuming agent, a surfactant and an emulsion stabilizer.

A preferred formulation of one composition according to the present invention includes per gallon: 12.32 g oxalic acid, 0.33 vol-% Silicone 47V350, 0.1 vol-% Silicone 10646 (an aminofunctional polysiloxane), 3.75 vol-% Silicone 4518, 0.76 vol-% Silane Z6070 (the foregoing silicones being products of Rhone-Poulenc, Inc. and the silane being a product of Ashland Chemical Co. of Columbus Ohio), 0.28 vol-% Acryloid B-67 (an acrylic polymer sold by Rohm & Haas), and 9.24 g $\text{SiF}_6\text{MgH}_2\text{O}$; a co-solvent system including 1.55 vol-% ethyl alcohol, 0.77 vol-% isopropyl alcohol, 20.69 vol-% propylene glycol ether monomethyl ether, 0.47 vol-% 1,1,1-trichloroethane, 0.38 vol-% trichlorotrifluoroethane, and 20 vol-% water; and as additives, orange oil terpene (a perfuming agent), and 0.4 vol-% nonylphenylpolyethoxylate (a surfactant). These components are mixed together under conditions effective to form an emulsion, such as with a conventional air blow mixer. Finally, 3 vol-% Michemlube 743 (a paraffin emulsion sold by Michelman, Inc. which acts as a stabilizer) is added to enhance the shine of the floor and as a fixative for the emulsion previously formed.

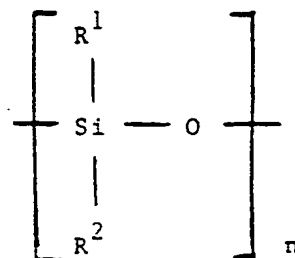
DETAILED DESCRIPTION OF THE INVENTION

The balanced compositions of the present invention generally include at least one, and optionally a plurality of, acidic cleaning agents, such as the polycarboxylic chelating acids. Additionally, the compositions include a plurality of silicones further including at least one aminofunctional polysiloxane and at least one silane which is believed to act as a cross-linking agent. The plurality of silicones should reflect different molecular weights and therefore different molecular sizes, so as to most effectively coat or fill the variously-sized cracks and depressions of the floor to be treated. An alkaline earth fluorosilicate is included to react chemically with mineralized or mineral-containing floors such as marble or vinyl composite floors, respectively. Additionally, a film-forming agent such as an acrylic resin is included to form a protective layer above the surface treated. A co-solvent system is also co-formulated, including at least one lower aliphatic alcohol, at least one glycol ether, at least one halogenated hydrocarbon, at least one non-halogenated hydrocarbon solvent and water. The glycol ether, for example, serves to help solubilize the silicone components of the formulation, as well as to clean the floor surface. Also, preferably co-formulated as additives are orange oil terpene which imparts a desirable odor to the ultimate composition, a surfactant and a stabilizing agent like Parrafin Emulsion (Michemlube 743 such as is sold by the Michelman Corp. of Cincinnati, Ohio) which is added to stabilize the emulsified product of the preceding ingredients.

The polycarboxylic chelating acids contemplated by the present compositions enhance the soil-removing ability thereof, and it is believed that they further cooperate with the polysiloxane constituents also present to contribute to a durable, water-repellent film on the treated surfaces. For this purpose, suitable acids are polycarboxylic chelating acids having a first pK value in the range of about 1 to about 3.5. Illustrative of such acids are citric acid (pK' 3.09), oxalic acid (pK' 1.25), ethylenediaminetetraacetic acid (pK' 2.00), and the like. The claimed compositions preferably include about 10 to about 100 g of oxalic acid per gallon of product, more preferably about 10 to about 20 g, and most preferably about 12 g, or, in other words about 0.2 to 2.2 molar equivalents of acid functionality per gallon of product, more preferably about 0.23 to 0.5 molar equivalents and most preferably about 0.26 molar equivalents of acid. It is contemplated that for particular floors, such as marble, the acid component may be omitted to avoid a bleaching effect. The proper amount of whichever acid is chosen can be adjusted to suit a particular floor surface by routine testing.

The contemplated silicones include organic polysiloxanes which are film formers having a vis-

cosity in the range of about 5 to about 50,000 centistokes, preferably about 100 to about 10,000 centistokes. More preferably, a mixture of polysiloxanes having relatively higher and relatively lower viscosities is employed. Such polysiloxanes have the repeating group



wherein n is an integer having a value greater than 1, R^1 is an alkyl radical containing 1 to 7 carbon atoms, inclusive, R^2 is a member of the group consisting of hydrogen, an alkyl radical containing 1 to 7 carbon atoms, inclusive, or a phenyl group.

Illustrative polysiloxanes encompassed by the above formula are polydimethylsiloxane, polydiethylsiloxane, polymethylethyl siloxane, polymethylphenyl siloxane, and copolymers of two or more of the foregoing siloxanes. Polysiloxane-oxalkylene block copolymers of the type described in U.S. Patent No. 3,306,869 to Lahr et al. may also be utilized.

The present compositions also include an aminofunctional polysiloxane as well as a silane. The amino-functional polysiloxane is a silicone fluid with highly polar pendant aminoalkyl modifying groups that enhance the durability of the film formed by the polysiloxanes present and promotes adhesion of the formed film to a wide variety of substrates.

Illustrative of the amino-functional polysiloxanes suitable for use in the present composition are the aminofunctional polydimethylsiloxane polymers commercially available under the designation Dow Corning 531 Fluid and Dow Corning 536 Fluid from Dow Corning Corporation, Midland, Michigan, the alkylene diamino-functional dimethylpolysiloxane fluid commercially available under the designation Silicone Fluid F-756 from Wacker Silicones Corporation, Adrian, Michigan, the aminofunctional polysiloxane fluid commercially available under the designation Rhodorsil Oil 10646 from Rhone-Poulenc, Inc., Monmouth Junction, New Jersey, and the like. The aminofunctional polysiloxanes are preferably incorporated in a range of about 0.05 to about 1 vol-%, preferably about 0.05 to about 0.4 vol-%, and most preferably about 0.1 vol-%.

Silicone Resin 47V350 is a polymethylsiloxane

which has a viscosity of 1,000 centistokes (cSt) at 25°C., is a 100% silicone fluid, and has a flash point of 570°F (299°C.). Silicone Resin 4518 is a methylpolysiloxane solution in mineral spirits which has a viscosity of 12 cSt at 25°C., a solids content of 70 percent by weight, and a flash point of 122°F (50°C). Silicone Resin 10646 is an aminofunctional polydimethylsiloxane, has a viscosity of 20 cSt at 25°C. and a flash point of 120°F (54°C.). Silicone Resins 47V350, 4518 and 10646 were obtained from Rhone-Poulenc, Inc., Monmouth Junction, N.J. under the trade name RHODORSIL. Other silicone ingredients are presented in U.S. Patent Nos. 4,212,759, 4,124,523 and 3,579,540, the disclosures of which are expressly incorporated herein by reference in their entireties.

As stated above, the present composition also contemplates an optional but preferred liquid silane constituent, which promotes the mutual solubility of the other organic silicone compounds present in the balanced solvent mixture utilized by the present compositions. Suitable liquid silanes are represented by the formula $R^3-Si(OR^4)_3$ wherein R^3 can be an alkyl radical containing one to three carbon atoms, inclusive or phenyl and R^4 can be an alkyl radical containing one or two carbon atoms, inclusive. Silanes are preferably incorporated in a range of about 0.3 to about 2.2 vol-%, more preferably in a range of about 0.4 to about 1.6 vol-%, and most preferably about 0.8 vol-%. Suitable silanes are alkyl trialkoxysilanes such as methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, and the like, and aryl trialkoxysilanes such as phenyltrimethoxysilane, phenyltriethoxysilane, and the like. An exemplary silane is Silane Z6070 (100% trimethylmethoxysilane sold by Ashland Chemical Co. of Columbus, Ohio).

Regardless of the individual silicones selected, the total contribution of all silicones (including silanes) to the compositions of the present invention is preferably about 1 to 6 vol-%, more preferably about 1 to about 3 vol-%, and most preferably about 1.2 vol-%.

Halogenated hydrocarbon cleaners (and solvents) that are suitable for compounding the present co-solvent system include 1,1,1-trichloroethane, 1,1,2-trichloroethane, trichlorotrifluoroethane, o-dichlorobenzene, alpha-chloronaphthalene and the like, as well as mixtures thereof. Trichlorotrifluoroethane is sold commercially under the trade name GENSOLVE D by Allied Chemical Co. of Morristown, New Jersey. Halogenated hydrocarbons are incorporated in a preferred range of about 0.4 to about 2 vol-%, more preferably about 0.6 to about 1.5 vol-%, and most preferably about 0.8 vol-%.

Suitable nonhalogenated hydrocarbon solvents

for co-solvent system of the present invention are those having a kauri-butanol value of about 20 to about 50 and a boiling point of about 80°C to about 200°C. The "kauri-butanol value" is a measure of the solvent power of the hydrocarbon liquid. Kauri gum is readily soluble in butanol but insoluble in hydrocarbons, thus this value is the measure of the volume of solvent required to produce turbidity in a standard solution containing kauri gum dissolved in butanol. Naphtha fractions have a kauri butanol value of about 30 and toluene about 150.

Illustrative suitable hydrocarbon solvents are mineral spirits, high flash naphtha, kerosene, Standard solvent, isoparaffinic hydrocarbon solvents, and the like. Illustrative isoparaffinic solvents that are substantially odor-free are those commercially available under the designation ISOPAR from Exxon Chemical Company, Houston, Texas, and under the designation SOLTROL from Phillips Petroleum Corporation, Bartlesville, Oklahoma. The non-halogenated hydrocarbon solvents are preferably present in a range of about 13 to about 70 vol-%, more preferably, in a range of about 30 to about 50 vol-%, and most preferably about 45 vol-%.

Suitable lower aliphatic alcohols for the present system of co-solvents are ethanol, isopropanol, n-propanol, sec-butanol, n-butanol, hexanol, cyclohexanol and the like, and mixtures thereof. These alcohols are preferably present in a range of about 1.5 to about 12 vol-%, more preferably in a range of about 2 to about 7 vol-%, and most preferably about 2.5 vol-%.

Illustrative glycol ethers are the alkylene glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, ethylene glycol monoisobutyl ether, diethylene glycol monoisobutyl ether, propylene glycol monoisobutyl ether, ethylene glycol monophenyl ether, propylene glycol monophenyl ether, and the like and mixtures of the foregoing. Glycol ethers are preferably present in a range of about 8 to about 30 vol-%, more preferably in a range of about 15 to about 25 vol-%, and most preferably about 21 vol-%. Particularly for treatment of vinyl floors, where glycol ethers may cause excessive bleaching, glycol ether may be omitted. In such a case, an offsetting amount of the nonhalogenated hydrocarbon solvent may be added in its place.

Water is also an ingredient of the co-solvent system of the present invention. It functions to solubilize water-based stains and also serves to dilute certain of the other cleaners and solvents such as the glycol ethers which might otherwise tend to discolor certain floors such as vinyl. Water

is preferably present in a range of about 10 to about 40 vol-%, more preferably in a range of about 15 to about 30 vol-%, and most preferably about 20 vol-%.

The formulations of the present invention also include an acrylic co-polymer such as the Rohm & Haas product Acryloid B-67 which is an isobutyl methacrylate polymer. Such an acrylic polymer contributes to an enhanced shine, but must be present in a relatively small amount so as to minimize the build-up of an acrylic surface that would otherwise require the stripping of the entire floor-protecting layer. Alternative acrylic resins will be readily known to workers in the field. The acrylic component of the floor treatment products of the present invention is preferably present, taking Acryloid B-67 as an example, in about 0.3 to about 1.5 vol-%, more preferably in a range of about 0.5 to about 1 vol-%, and most preferably about 0.8 vol-%.

The floor treatment compositions of the present invention also include an emulsion stabilizing ingredient. Particularly contemplated for this purpose is a nonionic paraffin wax emulsion sold by Michelman, Inc. of Cincinnati, Ohio under its Michemlube trademark. This product very surprisingly serves a dual function in the formulation of the present invention, by participating in forming a protective film along with the silicones and acrylic resin and by stabilizing the emulsion formed by the overall composition. Most particularly contemplated is the Michemlube 743 Paraffin Emulsion which is an emulsion of a 147° F melting point fully-refined paraffin wax. Also contemplated for use as an emulsion stabilizer is Michemlube 723 which is a lower melting point version of Michemlube 743. Taking Michemlube 743 as an example, the compositions of the present invention preferably include about 1.3 to about 6.6 vol-%, more preferably about 2 to about 4 vol-%, and most preferably about 3 vol-% of this stabilizer.

An additional ingredient of the floor treatment compositions of the present invention is an alkaline earth fluorosilicate such as SiNa_2F_6 , SiMgF_6 and SiCaF_6 which are representative compounds. These fluorosilicates may be utilized in their hydrated form, and the particular fluorosilicate selected is not critical so long as it possesses a reactivity with the calcium carbonate moieties exposed on the surface of marble flooring or vinyl-mineral composite flooring. Taking $\text{SiMgF}_6\text{H}_2\text{O}$ as an example, the compositions of the present invention preferably include about 5 to about 30 g/gallon, more preferably about 7 to about 25 g/gallon and most preferably about 15 g/gallon of fluorosilicate.

The foregoing compositions preferably also include additives such as a terpene hydrocarbon, e.g., orange oil terpene [1-methyl-4-(1-

methylethenyl)-cyclohexene] for fragrance, dyes as may be conventionally added when required, other fragrances, and the like. When added, the fragrance, using orange oil terpene as an example, preferably include about 2.5 to about 10 vol-%, more preferably about 4 to about 8 vol-%, and most preferably about 5 vol-% of this ingredient. The compositions also preferably include a surface-active agent or surfactant, particularly having a detergent function, such as nonyl-phenol polyethoxylate, containing an average of about 9.5 ethylenoxy groups per molecule, as is sold by the Thompson-Hayward Chemical Co. under the tradename T-DET N9.5. When added, the surfactant should be present in an amount sufficient to facilitate the blending of ingredients into an emulsion. Using T-DET N9.5 as an example, the surfactant is preferably added in a range of about 0.2 to about 0.4 vol-%, more preferably about 0.25 to about 0.35 vol-%, and most preferably about 0.3 vol-%.

While the following examples contemplate the complete formulation of products according to the present invention, they may be alternatively formulated where shipping constraints are present. Thus, in lieu of mixing all of the ingredients at one time, the non-solvent ingredients may be premixed in two separate containers. Thus, the acid and silicones may be mixed together, and separately mixed and contained are the fluorosilicates, surfactants, silanes, acrylic resins, paraffin emulsion stabilizer and perfumes or dyes. These products can be shipped to other geographic areas, at which time the water and remaining co-solvent system members would be added to a mixture of the foregoing non-solvent ingredients. When the complete formulation is made up as per the Examples which follow, the organic, nonwater liquids form a clear solution. Upon the addition of water followed by mixing, a milky emulsion forms.

The following examples are thus to be considered as illustrative only, and are not to be considered as limitative in any manner of the claims which follow. For example, it is contemplated that one of ordinary skill in the art can select, without undue experimentation, alternative ingredients from the foregoing discussion to particular compounds formulated together as follows.

Example 1

One gallon of a formulation according to the present invention (or approximately 3,776 ml) was prepared with the following ingredients. In a two gallon tank was added 12.32 g oxalic acid, 58.52 ml ethyl alcohol, 28.95 ml isopropyl alcohol, 12.32 ml Silicone 47V350, 3.78 ml Silicone 10646, 14.17

ml Silicone 4518, 781.40 ml propylene glycol monomethylether, 1,713 ml odorless mineral spirits, 17.56 ml 1,1,1-trichloroethane, 14.48 ml GENSOLVE D, 203.59 ml orange oil terpene, 28.92 ml Silane Z6070, 755.20 ml water, 30.80 ml Acryloid B-67 and 9.24 g $\text{SiF}_6\text{MgH}_2\text{O}$. The foregoing ingredients were further blended for 2 hours in a conventional air blower mixer. Finally, 113.28 ml of Paraffin Emulsion Michemlube 743 were added to the other ingredients in the mixer to fix the emulsion. After 2 more hours the formulation was bottled.

Example 2

One gallon of a formulation according to the present invention (or approximately 3,776 ml) can be prepared with the following ingredients. In an appropriately sized reaction vessel, add 12.9 g oxalic acid, 120 ml ethyl alcohol, 25 ml isopropyl alcohol, 10.0 ml Silicone 47V350, 2.0 ml Silicone 10646, 10.0 ml Silicone 4518, 300 ml ethylene glycol monoethylether ether, 2,361 ml mineral spirits, 37.8 ml GENSOLVE D, 100 ml orange oil terpene, 45.0 ml Silane Z6070, 700.0 ml water, 15.0 ml Acryloid B-67 and 30.0 g $\text{SiF}_6\text{CaH}_2\text{O}$. The foregoing ingredients are blended for about 2-2½ hours in a conventional air blower mixer to form an acceptable emulsion. Finally, 50.0 ml of Paraffin Emulsion Michemlube 743 are added to the other ingredients in the mixer to fix the emulsion. After 2 more hours the formulation can be decanted.

Example 3

One gallon of a formulation according to the present invention (or approximately 3,776 ml) can be prepared with the following ingredients. In an appropriate reaction vessel, add 20.0 g oxalic acid, 140 ml hexanol, 20.0 ml isopropyl alcohol, 15.0 ml Silicone 47V350, 11.0 ml Silicone 10646, 5.0 ml Silicone 4518, 350 ml diethylene glycol monoethylether, 2,311 ml odorless mineral spirits, 15.0 ml 1,1,2-trichloroethane, 20.0 ml GENSOLVE D, 50.0 ml orange oil terpene, 65.0 ml Silane Z6070, 675 ml water, 19.0 ml Acryloid B-67, 25.0 g $\text{SiF}_6\text{MgH}_2\text{O}$ and 12 ml T-DET N9.5. The foregoing ingredients are further blended for 2-2½ hours in a conventional air blower mixer until an emulsion has been formed. Finally, 75.0 ml of Paraffin Emulsion Michemlube 743 are added to the other ingredients in the mixer to fix the emulsion. After 1½ - 2 more hours the formulation is completed.

Example 4

One gallon of product can be formulated with 25.0 g oxalic acid, 150 ml ethyl alcohol, 35.0 n-propanol, 20.0 ml Silicone 47V350, 8.0 ml Silicone 10646, 20.0 ml Silicone 4518, 400 ml ethylene glycol mono-n-butylether, 1,995 ml odorless mineral spirits, 16.5 ml 1,1,1-trichloroethane, 21.0 ml GENSOLVE D, 120 ml orange oil terpene, 20.0 ml Silane Z6070, 800 ml water, 21.0 ml Acryloid B-67 and 20 g $\text{SiF}_6\text{Na}_2\text{H}_2\text{O}$. The foregoing ingredients can be blended for about 2 hours in a conventional air blower mixer. Finally, 150 ml of Paraffin Emulsion Michemlube 743 are added to the other ingredients in the mixer to fix the emulsion. After about 2 more hours the formulation is complete.

Example 5

Approximately 3,776 ml (about one gallon) of a product encompassed by the claimed invention may be prepared with the following ingredients. In a two gallon tank, add 40.0 g oxalic acid, 160 ml sec-butanol, 40 ml isopropyl alcohol, 30.0 ml Silicone 47V350, 12.0 ml Silicone 10646, 25.0 ml Silicone 4518, 500 ml propylene glycol monomethylether, 1,904 ml odorless mineral spirits, 17.0 ml 1,1,1-trichloroethane, 20.0 ml GENSOLVE D, 200 ml orange oil terpene, 25.0 ml Silane Z6070, 600 ml water, 33 ml Acryloid B-67, 10.0 g $\text{SiF}_6\text{Na}_2\text{H}_2\text{O}$ and 10.0 ml T-DET N9.5. Blend the foregoing ingredients for about 1½ - 2½ hours in a conventional air blower mixer and afterwards add 200 ml of Paraffin Emulsion Michemlube 723 to fix the emulsion. After about 2 more hours, the formulation is completed.

Example 6

One gallon of a formulation according to the present invention (or approximately 3,776 ml) is prepared as follows. In a conventional aeration mixer, combine 100 g oxalic acid, 300 ml ethyl alcohol, 35.0 ml Silicone 47V350, 16.0 ml Silicone 10646, 30.0 ml Silicone 4518, 800 ml propylene glycol monomethylether, 1,166 ml odorless mineral spirits, 19.0 ml 1,1,1-trichloroethane, 18.0 ml GENSOLVE D, 250 ml orange oil terpene, 65.0 ml Silane Z6070, 800 ml water, 25.0 ml Acryloid B-67, 10 g $\text{SiF}_6\text{MgH}_2\text{O}$ and 10 g SiNa_2F_6 . Blend the foregoing ingredients together for about 2 - 2½ hours in a conventional air blower mixer and then add 250 ml of Paraffin Emulsion Michemlube 743 to fix the emulsion. After about 2 more hours, decant the complete formulation.

Example 7

About one gallon of a formulation according to the present invention (or approximately 3,776 ml) is prepared with the following ingredients. In a two gallon tank add 10.0 g citric acid, 100 ml ethyl alcohol, 20.0 ml isopropyl alcohol, 40.0 ml Silicone 47V350, 20.0 ml Silicone 10646, 35.0 ml Silicone 4518, 950 ml propylene glycol monomethylether, 519 ml odorless mineral spirits, 20.0 ml 1,1,1-trichloroethane, 17.0 ml GENSOLVE D, 300 ml orange oil terpene, 1,450 ml water, 40.0 ml Acryloid B-67, 10.0 g $\text{SiF}_6\text{MgH}_2\text{O}$ and 15.0 ml T-DET N9.5. The foregoing ingredients are further blended for about 2 hours in a conventional air blower mixer. Finally, 250 ml of Paraffin Emulsion Michemlube 743 are added to the other ingredients in the mixer to fix the emulsion. After 2 more hours the formulation is decanted and bottled.

Example 8

About one gallon of a formulation according to the present invention (or approximately 3,776 ml) may be prepared according to the following protocol. Note that the glycol ether is omitted for those floors, such as dark vinyl or particular old floors, in which an undesirable amount of bleaching would otherwise be present. In an appropriate mixing vessel, add 20.0 g citric acid, 120 ml ethyl alcohol, 12.0 ml Silicone 47V350, 22.0 ml Silicone 10646, 40.0 ml Silicone 4518, 1,998 ml odorless mineral spirits, 25.0 ml 1,1,1-trichloroethane, 12.0 ml GENSOLVE D, 285 ml orange oil terpene, 1,000 ml water, 42.0 ml Acryloid B-67 and 20.0 g $\text{SiF}_6\text{MgH}_2\text{O}$. The foregoing ingredients should be blended for 2 hours in a conventional air blower mixer. Finally, 200 ml of Paraffin Emulsion Michemlube 743 should be added to the other ingredients in the mixer to fix the emulsion. After 2 more hours the formulation will be completed.

Example 9

Approximately one gallon of a formulation according to the present invention can be prepared, omitting the glycol ether where its presence has an excessive bleaching effect on a particular floor, with the following ingredients. In a two gallon tank, add 10.0 g phosphoric acid, 140 ml ethyl alcohol, 13.0 ml Silicone 47V350, 24.0 ml Silicone 10646, 45.0 ml Silicone 4518, 2,672 ml odorless mineral spirits, 30.0 ml 1,1,1-trichloroethane, 7.0 ml GENSOLVE D, 180 ml orange oil terpene, 500 ml water, 45.0 ml Acryloid B-67, 25.0 g $\text{SiF}_6\text{MgH}_2\text{O}$ and 20 ml T-DET N9.5. The foregoing ingredients are further blended for $1\frac{1}{2}$ - $2\frac{1}{2}$ hours in a conventional air blower mixer. Finally, 100 ml of Paraffin Emulsion

Michemlube 723 are added to the other ingredients in the mixer to fix the emulsion. After about $1\frac{1}{2}$ - 2 more hours the formulation may be decanted and bottled.

Example 10

For maintenance of marble surfaces, the acid component may be reduced or optionally omitted. Accordingly, one gallon of a formulation according to the present invention can be prepared as follows. In a two gallon tank, add 150 ml ethyl alcohol, 18.0 ml Silicone 47V350, 28.0 ml Silicone 10646, 50.0 ml Silicone 4518, 2,712 ml odorless mineral spirits, 38.0 ml 1,1,1-trichloroethane, 80.0 ml Silane Z6070, 600 ml water, 50.0 ml Acryloid B-67 and 30.0 g $\text{SiF}_6\text{MgH}_2\text{O}$. The foregoing ingredients are blended for 2 hours in a conventional air blower mixer and 50.0 ml of Paraffin Emulsion Michemlube 743 is added to the other ingredients in the mixer to fix the emulsion. After 2 more hours the formulation may be bottled or otherwise packaged.

From the foregoing detailed description and Examples, it will be apparent to those skilled in the art that various modifications and variations could be made in the selection of specific ingredients and overall product formulations of the present invention without departing from the scope or spirit of the claims which follow. It is expressly contemplated, for example, that reduced levels of acid or glycol ether may be incorporated for treatment of primarily marble floors or dark vinyl floors, respectively, to avoid bleaching effects. Similarly, increased proportions of fragrances may be added for treatment compositions used primarily for indoor floors or public area. The present invention is thus not limited to the foregoing examples, but is broadly encompassing of the following claims and equivalents thereto.

Claims

1. A floor treatment emulsion comprising at least one polycarboxylic chelating acid capable of cleaning the floor and imparting an enhanced shine thereto, a plurality of silicones, including at least one aminofunctional polysiloxane, capable of coating the floor surface and of imparting water repellency thereto, at least one lower aliphatic alcohol, at least one halogenated hydrocarbon and one nonhalogenated hydrocarbon solvent, water, at least one alkaline earth fluorosilicate compound capable of chemically reacting with calcium carbonate exposed on the surface of the floor, at least one film-forming acrylic resin, and at least one

emulsion-stabilizing agent capable of stabilizing an emulsion formed by the foregoing ingredients.

2. The floor treatment emulsion of claim 1, wherein said plurality of silicones further comprises at least one silane.

3. The floor treatment composition of claim 2, wherein said at least one acid is selected from the group consisting of citric acid, oxalic acid and ethylenediaminetetracetic acid; said at least one silicone is selected from the group consisting of polydimethylsiloxane, polydiethylsiloxane, polymethylethyl siloxane, polymethylphenyl siloxane, and copolymers of two or more of the foregoing siloxanes; said at least one silane is selected from the group consisting of methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, phenyltrimethoxysilane and phenyltriethoxysilane; said at least one hydrocarbon solvent is selected from the group consisting of mineral spirits, high-naptha, kerosene, Stoddard solvent, isoparaffinic hydrocarbon solvents and said halogenated hydrocarbon solvent is selected from the group consisting of 1,1,1-trichloroethane, 1,1,2-trichloroethane, trichlorotrifluoroethane, O-dichlorobenzene, alpha-chloronaphthalene; said at least one lower aliphatic alcohol is selected from the group consisting of ethanol, isopropanol, n-propanol, sec-butanol, n-butanol, hexanol, cyclohexanol and mixtures thereof, and said at least one fluorosilicate compound is selected from the group consisting of SiMgF_6 , SiNa_2F_6 , SiCaF_6 , and hydrates thereof.

4. The floor treatment emulsion of claim 2, further comprising a glycol ether.

5. The floor treatment emulsion of claim 4, wherein said glycol ether is selected from the group consisting of ethylene glycol monomethyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, ethylene glycol monoisobutyl ether, diethylene glycol monoisobutyl ether, propylene glycol monoisobutyl ether, ethylene glycol monophenyl ether and propylene glycol monophenyl ether.

6. The floor treatment emulsion of claim 5, further comprising a surfactant.

7. A floor treatment emulsion consisting essentially of a polycarboxylic chelating acid, a plurality of silicones including at least one aminofunctional polysiloxane, at least one lower aliphatic alcohol, at least one halogenated and one nonhalogenated hydrocarbon solvent, water, at least one alkaline earth fluorosilicate compound, at least one film-forming acrylic resin and at least one emulsion stabilizing agent.

8. The floor treatment emulsion of claim 7,

wherein said plurality of silicones further includes at least one silane.

9. The floor treatment emulsion of claim 8, wherein said at least one acid is selected from the group consisting of citric acid, oxalic acid and ethylenediaminetetracetic acid; said at least one silicone is selected from the group consisting of polydimethylsiloxane, polydiethylsiloxane, polymethylethyl siloxane, polymethylphenyl siloxane, and copolymers of two or more of the foregoing siloxanes; said at least one silane is selected from the group consisting of methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, phenyltrimethoxysilane and phenyltriethoxysilane; said at least one hydrocarbon solvent is selected from the group consisting of mineral spirits, high-naptha, kerosene, Stoddard solvent, isoparaffinic hydrocarbon solvents and said halogenated hydrocarbon solvent is selected from the group consisting of 1,1,1-trichloroethane, 1,1,2-trichloroethane, trichlorotrifluoroethane, O-dichlorobenzene, alpha-chloronaphthalene; said at least one lower aliphatic alcohol is selected from the group consisting of ethanol, isopropanol, n-propanol, sec-butanol, n-butanol, hexanol, cyclohexanol and mixtures thereof; and said at least one fluorosilicate compound is selected from the group consisting of SiMgF_6 , SiNa_2F_6 , SiCaF_6 and hydrates thereof.

10. The floor treatment emulsion of claim 9, further including a glycol ether.

11. The floor treatment emulsion of claim 10, wherein said glycol ether is selected from the group consisting of ethylene glycol monomethyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, ethylene glycol monoisobutyl ether, diethylene glycol monoisobutyl ether, propylene glycol monoisobutyl ether, ethylene glycol monophenyl ether and propylene glycol monophenyl ether.

12. The floor treatment emulsion of claim 11, further including a surfactant.

13. A floor treatment emulsion comprising about 0.2 about to about 2.2 molar equivalents of acid functionality of a polycarboxylic chelating acid, about 1 to about 6 vol-% of a plurality of silicones including about 0.05 to about 1 vol-% of an aminofunctional polysiloxane and about 0.3 to about 2.2 vol-% of a silane, about 1.5 to about 12 vol-% of a lower aliphatic alcohol, about 0.4 to about 2 vol-% of a halogenated hydrocarbon solvent and about 13 to about 70 vol-% of a non-halogenated hydrocarbon solvent, about 10 to about 40 vol-% water, about 5 to about 30 g/gallon of an alkaline earth fluorosilicate, about 0.3 to about

1.5 vol-% of a film-forming acrylic resin, an emulsion-stabilizing amount of an emulsion stabilizer, a surfactant and a fragrance.

14. The floor treatment emulsion of claim 13 further comprising about 8 to about 30 vol-% of a glycol ether. 5

15. The floor treatment emulsion of claim 13 further comprising about 0.23 to about 0.5 molar equivalents of acid functionality of a polycarboxylic chelating acid, about 1 to about 3 vol-% of a plurality of silicones including about 0.05 to about 0.4 vol-% of an aminofunctional polysiloxane and about 0.4 to about 1.6 vol-% of a silane, about 2 to about 7 vol-% of a lower aliphatic alcohol, about 0.6 to about 1.5 vol-% of a halogenated hydrocarbon solvent and about 30 to about 50 vol-% of a nonhalogenated hydrocarbon solvent, about 15 to about 30 vol-% water, about 10 to about 20 g/gallon of an alkaline earth fluorosilicate, about 0.5 to about 1 vol-% of a film-forming acrylic resin, an emulsion-stabilizing amount of an emulsion stabilizer, a surfactant and a fragrance. 10 15 20

16. The floor treatment emulsion of claim 15 further comprising about 15 to about 25 vol-% of a glycol ether. 25

17. The floor treatment emulsion of claim 15 further comprising about 0.26 molar equivalents of acid functionality of a polycarboxylic chelating acid, about 1.2 vol-% of a plurality of silicones including about 0.1 vol-% of an aminofunctional polysiloxane and about 0.8 vol-% of a silane, about 2.5 vol-% of a lower aliphatic alcohol, about 0.8 vol-% of a halogenated hydrocarbon solvent and about 45 vol-% of a nonhalogenated hydrocarbon solvent, about 20 vol-% water, about 15 g/gallon of an alkaline earth fluorosilicate, about 0.8 vol-% of a film-forming acrylic resin, an emulsion-stabilizing amount of an emulsion stabilizer, a surfactant and a fragrance. 30 35

18. The floor treatment emulsion of claim 17 further comprising about 21 vol-% of a glycol ether. 40

19. A floor treatment emulsion comprising per gallon: about 12.3 g oxalic acid, 0.3 vol-% Silicone 47V350, 0.1 vol-% Silicone 10646, 3.8 vol-% Silicone 4518, 0.8 vol-% Silane Z6070, 0.3 vol-% Acryloid B-67, and 9.2 g $\text{SiF}_6\text{MgH}_2\text{O}$; a co-solvent system including 1.6 vol-% ethyl alcohol, 0.8 vol-% isopropyl alcohol, 21 vol-% propylene glycol ether monomethyl ether, 0.5 vol-% 1,1,1-trichloroethane, 0.4 vol-% trichlorotrifluoroethane, and 20 vol-% water; and as additives, 5 vol-% orange oil terpene, 0.4 vol-% nonylphenylpolyethoxylate and 3 vol-% Michemlube 743. 45 50

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(54) **Floor treatment product.**

(57) An emulsified, balanced floor treatment product is provided having a plurality of cleaning agents, including acids, alcohols, hydrocarbon solvents, water, a plurality of silicone components, at least one fluorosilicate compound capable of reacting with calcium carbonate, and at least one emulsion-stabilizing agent.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 263 959 (HENKEL) * claim 1 * ---	1	C 11 D 7/14 C 11 D 7/24 C 11 D 7/30
A	EP-A-0 171 122 (THE PROCTER & GAMBLE) * claim 1 * ---	1	C 11 D 7/22 C 11 D 7/50
A	CH-A- 473 207 (REICHOLD CHEMIE) * claims 1,2 * ---	1	C 09 G 1/10 C 09 G 1/12
A	US-A-3 785 860 (R.E. ZDANOWSKI) * claim 1 * ---	1	
A	DE-B-2 721 573 (METALLGESELLSCHAFT) * examples 1,4 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 09 G 1/10 C 09 G 1/12 C 11 D 3/08 C 11 D 3/16 C 11 D 3/18 C 11 D 3/20 C 11 D 3/37 C 11 D 3/43 C 11 D 7/14 C 11 D 7/22 C 11 D 7/24 C 11 D 7/26 C 11 D 7/30 C 11 D 7/50
The present search report has been drawn up for all claims			
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